

Gas Law And Absolute Zero

Equipment: Safety gloves, Safety Glasses, Gas bulb with Pressure Gauge, $-10^{\circ}C$ to $+110^{\circ}C$ Thermometer, $-100^{\circ}C$ to $+50^{\circ}C$ Thermometer.

Caution: This experiment deals with materials that are very hot and very cold. Exercise care when handling these materials. Do not let them get in contact with your skin or clothes. Wear safety goggles to protect your eyes from splashes.

1 Purpose

To investigate how the pressure of a given quantity of gas in a fixed volume varies with the temperature. This relationship between pressure and temperature, which is approximately linear for low number densities and temperatures somewhat above liquefaction, is extrapolated to zero pressure. The temperature at which this occurs is absolute zero.

2 Description

See Fig. 1. A steel bulb is filled with air at ambient air pressure. The bulb is fitted with a pressure gauge that gives the absolute pressure inside the bulb in lb/in^2 . When the valve is opened, the pressure gauge gives the nominal outside air pressure, about $15 lb/in^2$. With the valve closed the bulb is inserted into 4 liquids of different temperatures. For each liquid, the temperature and pressure are measured. There are 5 pairs of pressure and temperature measurements. These are plotted on a graph and the best straight line is drawn. The straight line is extrapolated to zero pressure. The temperature at that point is determined and is absolute zero.

3 Theory

In an ideal gas, the molecules are considered so small that they can be approximated as point masses. For simplicity, we let the term molecules also include atoms. It is assumed that there are no forces between the molecules and that the energy of the gas is entirely the kinetic energy of the molecules. The molecules are in constant motion and as they bounce off the walls of the container, they exert a pressure (a force per unit area) on the walls. On a very short time scale, the pressure fluctuates a great deal, but on a longer time scale, the pressure fluctuations average out. The average kinetic energy of the molecules increases with the temperature, and the higher the temperature, the faster the molecules move. The pressure exerted by the gas will increase as the temperature rises because the molecules

move faster and hit the wall harder and more often. It is found that the pressure p and Temperature T_C obey a linear relationship that can be written as

$$p = mT_C + b, \quad (1)$$

where m and b are constants and T_C is the centigrade temperature.

No gas is strictly ideal and there will be deviations from Eq.(1), particularly as the gas becomes more dense and/or the temperature is decreased. But for dilute gases at high enough temperatures this equation is a good approximation. As the temperature decreases most gases will eventually become liquid and Eq.(1) is not valid. If data in the range where Eq.(1) is valid is extrapolated to $p = 0$, the very low temperature at which this occurs is independent of the gas used and is termed absolute zero. According to Eq.(1) absolute zero occurs at the centigrade temperature $T_C = -\frac{b}{m} = -273.15$. There is no temperature colder than absolute zero! If the kelvin temperature T is defined as $T = T_C + \frac{b}{m}$, Eq.(1) can be written as

$$p = mT. \quad (2)$$

What should the “constant” m be, and is it a constant for all situations?

Following is a rough derivation. Let the number density (number of molecules per unit volume) of the gas molecules be n_N . The number of molecules striking per unit area of the container wall per unit time is $n_N v$, where v is a suitable average speed of the molecules. The momentum carried by each molecule is proportional to Mv , where M is the mass of the molecule. The momentum carried toward the wall per unit area per unit time is proportional to $n_N Mv^2$, and the momentum carried away from the wall per unit area per unit time the same value. The net momentum transferred to the wall per unit area per unit time will be proportional to $2n_N Mv^2$, and according to Newton’s 2nd law, is proportional to the pressure. But Mv^2 is proportional to the kinetic energy which in turn, according to kinetic theory, is proportional to the Kelvin temperature. We must have that the pressure is proportional to the product of the n_N and T , or

$$p = n_N kT, \quad (3)$$

where k is the proportionality constant and is called Boltzmann’s constant. For Eq.(3) to be written in this simple form without an additive constant on the right hand side, the temperature must be in kelvin. Note that one degree kelvin is equal to one degree centigrade. Let the volume of the gas be V and Avogadro’s number be N_A . If both the numerator and denominator of the right hand side of Eq.(3) are multiplied by V and N_A , this equation can be written

$$PV = nRT, \quad (4)$$

where n is the number of moles of the gas and $N_A k = R = 8.31 \text{ J/mole/K}$ is the gas constant. It is customary to write K for degrees kelvin rather than $^\circ K$ or deg K .

4 Experiment

1. Begin by depressing the pin inside the end of the valve attached to the bulb. This connects the bulb to the room air and sets the bulb pressure at one atmosphere. Do

not open the valve again. Tap the gauge gently with a fingernail to be sure that the needle is not sticking (a good procedure with any mechanical gauge), and record the value indicated by the pressure gauge in units of lb/in^2 . Also record the temperature in the room using the $-10^\circ C$ to $+110^\circ C$ thermometer. Be careful that your hand does not warm the bulb above room temperature.

2. Immerse the bulb in boiling water. Use the $-10^\circ C$ to $+110^\circ C$ thermometer to measure the temperature of the water. Do not let the thermometer touch the bottom or sides of the boiling water container, where the temperature may differ from that of the water. When equilibrium is reached (the pressure reading becomes constant), record the pressure and the temperature. Remove the bulb from the steam bath and allow it to reach room temperature. Check to see that the pressure reading is the same as it was before subjecting the gas to the boiling water. If it is significantly different you may have a leak.
3. Immerse the bulb in a water-ice mixture. Using the same procedures as before, measure the pressure and temperature using the same thermometer.
4. Note: In this part of the experiment, **do not use the same thermometer. You will break it.** Use the $-100^\circ C$ to $+50^\circ C$ thermometer. Immerse the bulb and thermometer in alcohol. At first, cool the alcohol by adding small chips of solid carbon dioxide. *Do not touch the chips with unprotected fingers!* As the temperature drops and the boiling becomes less violent, add larger pieces of the carbon dioxide. It should be possible to lower the temperature to about $-72^\circ C$. Record the pressure and temperature as before.
5. In this part of the experiment, **do not insert any thermometer as it will break.** Immerse the bulb in liquid nitrogen. Do this slowly to minimize violent boiling. Take care not to touch the liquid nitrogen or to be splashed by it. Assume the temperature is $-196^\circ C$. Allow the gas to reach equilibrium and record the pressure.
6. When the bulb returns to room temperature check to see if it returns to about its original pressure.

5 Data Analysis

Export your data and analyze it by using Python. You will create a graph display of Temperature vs Pressure and create a best fit straight line to the data points. It is necessary to Rewrite Eq.(1) as

$$T = \frac{1}{m}p - \frac{b}{m}. \quad (5)$$

The temperature T will be plotted on the vertical axis and the pressure p on the horizontal axis. The slope of the line is $\frac{1}{m}$ and the vertical axis intercept (when $p = 0$) is $-\frac{b}{m}$, which is the value of absolute zero. Plot your data and find the slope and vertical axis intercept. Attach the graph and your code to the report.

- **What are the dimensions of temperature?**

- List the units of temperature.
- **What are the dimensions of m and b ?**
- **What units of m and b are you using?** Hint: They are not the same.

6 Results

Discuss your results. Suggestions.

- How well do your data fit a straight line?
- What is your value for absolute zero in degrees centigrade ($-\frac{b}{m}$)? Do the units make sense?
- Since Boltzmann's constant $k = 1.38 \times 10^{-23} \text{ J/K}$, what is n_N for your experiment? Hint: k is given in S.I. units. Express m in S.I. units, and calculate the density in molecules per cubic meter. Envision, if you can, that number of molecules.
- The diameter of the bulb is about 10 cm. Neglecting the wall thickness of the bulb, and the volume of the connecting tubing and pressure gauge, about how many moles of air are you working with?
- One of the assumptions in your data analysis is that the density of the air in the bulb stays constant. How many reasons can you think of for this not to be so? What kind of errors might be introduced?

Exercise: Obtain Eq.(4) from Eq.(3).

7 Comment

You might think that at zero degrees Kelvin atomic and molecular motion ceases. This is not the case. There is still a little bit of motion to these particles at absolute zero which is called zero point energy.

One of the statements of the Heisenberg uncertainty principle of quantum mechanics is that for each linear dimension the product of the uncertainties in momentum and position of a particle must be greater than or equal to Planck's constant h divided by 2π or $h/2\pi \equiv \hbar$. For example, if the linear dimension is denoted by x and the uncertainties in position and momentum are denoted by Δx and Δp_x , then $\Delta x \Delta p_x \geq \hbar$. If the momentum were zero (no motion) its momentum would be known exactly (no uncertainty, $\Delta p_x = 0$) and we would have no idea where the particle was.

8 Finishing Up

Please leave your bench as you found it. Thank you.

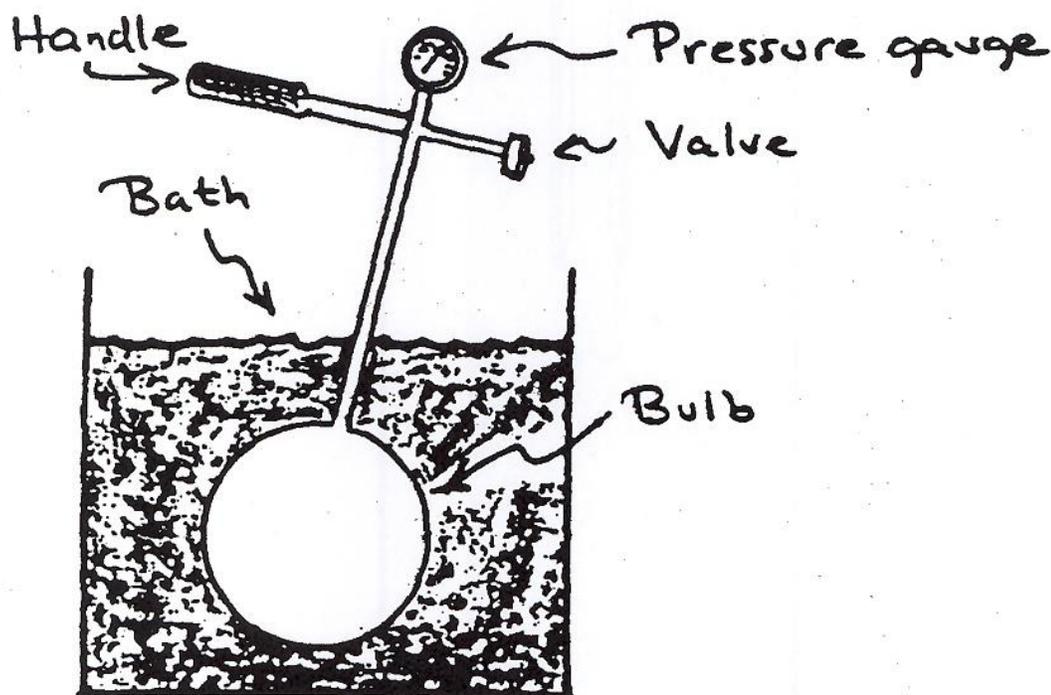


Figure 1: Fixed volume of gas in a constant temperature bath.